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CITATION:

ISHIHARA, Shigehisa ...[et al]. Fire Proofing Properties of Wood and Filter Paper treated with Cationic Melamine-Formaldehyde Condensation Products : Effect of Inorganic Acids on the Fire Proofing Efficiencies. Wood research : bulletin of the Wood Research Institute Kyoto University 1972, 52: 72-89

ISSUE DATE:

1972-01-31

URL:

<http://hdl.handle.net/2433/53416>

RIGHT:

# Fire Proofing Properties of Wood and Filter Paper treated with Cationic Melamine-Formaldehyde Condensation Products

—Effect of Inorganic Acids on the Fire Proofing Efficiencies\*—

Shigehisa ISHIHARA\*\* and Takamaro MAKU\*\*

**Abstract**—The durable fire-retardants based on the colloidal solution of cationic aminotriazinealdehyde resin have been applied to HINOKI sliced veneer and filter paper. The treatment is accomplished by soaking samples through an aqueous solution of these resins, drying and curing at room temperatures.

The effect of kind of acids and of varying ratio of fire retardant components in treating solution on the fire proofing efficiencies of HINOKI sliced veneer and filter paper are discussed.

Results are compared with those reported in previous paper<sup>4)</sup> and ammonium salts as fire retardant agents for wood, paper, fabrics and other combustible materials. Aminotriazine-aldehyde condensation products combined with strong acids such as phosphoric acid, hydrobromic acid, sulfuric acid and sulfamic acid imparted excellent fire resistance to wood and filter paper. Satisfactory fire proofing properties can be obtained in both HINOKI sliced veneer and filter paper at resin add-on as low as about 10~15% with a few exceptions. Total amount of resin required becomes lower as the melamine/acid ratio is decreased.

## Introduction

The processing of wood and cellulosic materials to impart fire retardancy has been studied in notable depth over the years. Considerable research is currently being carried out to impart to wood and cellulosic materials through chemical treatments such properties as durable fire resistance, water repellency and good dimensional stability<sup>1)</sup>. Because of economic considerations, the chemicals now used as fire retardants in wood and composite woods are inorganic salts such as mono- and diammonium phosphates, ammonium bromide, ammonium sulfamate, zinc chloride and borax-boric acid mixtures<sup>2)</sup>. Since they are soluble in water and are leachable and hygroscopic, they can neither improve dimensional stability nor impart decay resistance.

The durable fire retardants developed for wood and cellulosic materials in recent years have been based on organic phosphorus compounds, some of them

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\* Presented at 17th Annual Meeting of the Japan Wood Research Soc., Tokyo, Apr., 1967.

\*\* Division of Composite Wood.

also containing halogens. These compounds are converted upon polymerization or condensation to water-insoluble resins.

Methylol derivatives of aminotriazines may be modified by reaction with various compounds. These lead to the formation of ionic complexes or modified structures which adapt the polymers for specific uses<sup>3)</sup>. Phosphorus-containing organic compounds such as THPC (tetrakis(hydroxymethyl)phosphoniumchloride), NMPA (N-hydroxymethyl-3-(dialkylphosphone) propionamide<sup>23)</sup>) and the like which have methylol melamine incorporated in the polymers are known to have the excellent fire retarding properties. As described in previous paper<sup>4)</sup>, the cationic melamine-formaldehyde resin solution as a clear aqueous solution was prepared methylol derivatives of aminotriazines in presence of free acid as a component of fire retardant.

The fire proofing properties of wood and filter paper treated with the aqueous solution of phosphoric acid-containing aminotriazine-formaldehyde condensation products have been studied previously<sup>4)</sup>, but there have been no reports on the effectiveness of these resin containing other inorganic acids. The aim of the present work was to examine the possibility of producing a durable fire proofing treatment by causing wood or cellulose to react relatively simple compounds. The present paper reports experimental data which further define the effect of other inorganic acids in imparting fire proofing properties to wood and filter paper treated with the cationic melamine-formaldehyde resin. In the present paper further fire proofings effectiveness of various ammonium salts are discussed.

## Experimental

### Chemicals

Inorganic acids were the best grade commercial products.

Pure commercial melamine was recrystallized from water. The formaldehyde was the best grade formaline (ca. 37%). Ammonium salts were the best grade commercial one.

#### *Preparation of the cationic melamine-formaldehyde resin solutions*

A mixture of 1 mole of melamine, 3 moles formaldehyde and a certain mole (0.5, 1, 2 and 4 moles) of acid in 1000 ml water heated and stirred at 80°C under refluxing for 30 minutes, and diluted with water to obtain the various consistencies desired.

The ratio of acid to melamine in these resins varies with the type of acid used being, in general, greater for weaker acid such as phosphoric acid than for stronger ones such as hydrobromic acid and hydrochloric acid, but in all cases

Table 1. The optimum pH values and ratios of acid to melamine.

Acid	Mols acid per mole melamine	pH values* at 20°C
H <sub>3</sub> PO <sub>4</sub>	2.0~3.5	1.5
H <sub>2</sub> SO <sub>4</sub>	0.5~1.0	less than 2.5
H <sub>2</sub> NSO <sub>2</sub> OH	3.0	0.5
HCl	0.7~1.5	less than 2.0
HBr	0.7~2.0	"
H <sub>3</sub> BO <sub>3</sub> **	0.5~0.7	4.0

\* 17.8% of an aqueous solution of trimethylolmelamine.

\*\* Aqueous solution of H<sub>3</sub>BO<sub>3</sub>-containing resins were prepared at 45°C.

the pH range lies between about 0.5~4.5. The optimum values and acid ratios typical acids used in this study are shown in Table 1. These products were analyzed by the conventional method<sup>4,5</sup>).

### Specimens

#### *Filter paper*

Filter paper used in this study was the Toyo qualitative filter paper No. 2, with 110 g/m<sup>2</sup> of weight, 0.26 mm of thickness. The content of  $\alpha$ -cellulose and ash were 95% and up and 0.1 of the filter paper, respectively. Copper value of this filter paper was 1.0 max. and pH value was 6.8.

#### *Wood*

Sliced veneer of 0.34 mm thick used in this study were HINOKI (*Chamaecyparis obtusa* ENDL.) with an average specific gravity of 0.42 (on an oven-dried basis) and an average annual ring density of 9.0. These sliced veneer were edge grain and sapwood.

Dimension of specimens used in the flammability test were 0.34 mm (HINOKI) and 0.26 mm (filter paper) by 8.0 cm by 21.0 cm.

### Treatments of specimens

*Cationic melamine-formaldehyde condensation products:* Specimens of HINOKI sliced veneer and filter paper were treated by soaking with an aqueous solution of a resin as described above for 30~60 minutes at room temperatures, and then dried in the draught chamber for 71 hours at room temperatures. The dried specimens were cured for 5 weeks at room temperatures.

*Ammonium salts:* The same specimens as described above were soaking with an aqueous solution of an ammonium salt for 60 minutes at room temperatures (treating temperature of ammonium pentaborate was kept at 60°C.), and then dried in the draught chamber for 71 hours at room temperatures. Thereafter, they were dried for 20 hours at 60°C in a vacuum oven and then weighed. (Data reported are

3~10 specimens.)

*A resin add-on of treated samples* was controlled by varying the concentration of the treating solution with a given the molar ratios of the components.

*Caluculation of retentions* are based on the oven dry weight of the specimens as weighed.

#### Analytical methods

*Nitrogen.* Standard micro Dumas method (Coleman Nitrogen Analyser)

*Phosphorus.* The sample was burned with oxygen flask combustion method and the phosphate determined colorimetrically as the molybdenum blue complex.

*Sulfur.* Oxygen flask combustion followed by barium perchlorate method.

*Halogens.* Potentiometric titration method.

*Boron.* Atomic absorption technique.

#### Flammability test

Modified ASTM D 777-46, "Standard Methods of the Flammability for Treated Paper and Paperboard" was used to give a measure of the flammability of the vertical paper and paperboard with less than 1/16 in. of thickness. This flammability test was detailed in previous paper<sup>4)</sup>.

A sample of HINOKI sliced veneer or filter paper was held vertically in a draught-free enclosure. A Bunsen burner (1.1 cm in diameter) luminous flame, 3.1 cm in height, was applied to the bottom of each samples for 12 seconds, and then removed. Any flaming after the removal of the burner, and any after-glow, were noted, together with the length of char produced.

### Results and Discussion

#### *Hydrogen bromide-containing melamine-formaldehyde condensation products*

Effect of varying the ratio of hydrogen bromide-melamine in treating solution on the flammability of both HINOKI sliced veneer and filter paper were discussed. The molar ratios of the two active components in treating solution were varied, in order to establish the optimum for imparting both resistances of flaming and glowing combustions.

Fig. 1 shows that char-length data of treated HINOKI sliced veneer were significantly affected by varying the molar ratios of components in the treating solution. As shown in Figs. 1 and 2, it is apparent that lower resin add-ons of HINOKI sliced veneer and filter paper treated with the solution of higher hydrobromic acid molar ratio were sufficient to the excellent fire proofing efficiency to all treated specimens as measured by char length. For both specimens of HINOKI sliced veneer and filter paper treated with the solution with a higer hydrobromic acid molar

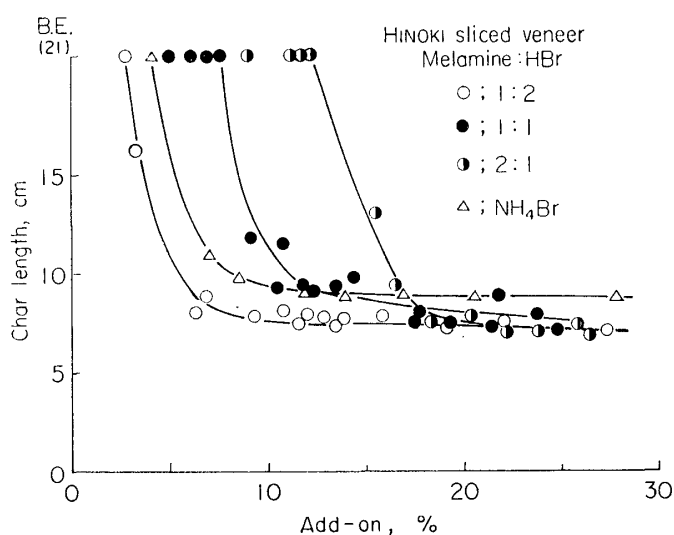


Fig. 1. Effect of HBr-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/HBr molar ratios. (B.E.=Burned Entire Length)

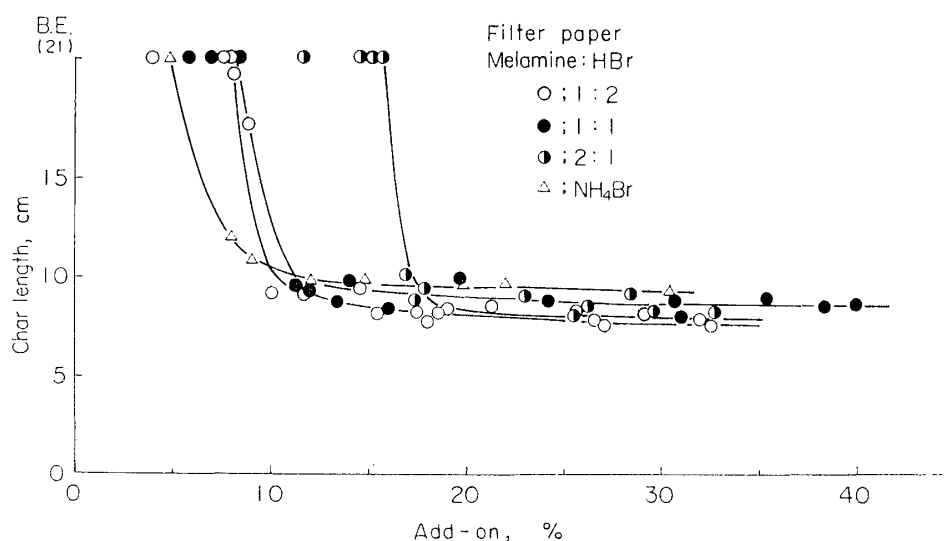


Fig. 2. Effect of HBr-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/HBr molar ratios. (B.E.=Burned Entire Length)

ratio of resin (melamine/HBr:1/2), the minimum resin add-ons necessary to pass the vartical flames test were about 6.0 and 10.0% respectively. Fire proofing efficiencies increased as the ratio of hydrobromic acid increased and in proportion with increasing resin add-on of the treated samples. Bromine-containing compounds appears to be principally effective in ignition stage of the burning process, by blocking access of oxygen and heat, and in combustion stage, by influencing the reactions of combustion. Bromine also is believed to perform most of its flame

retardant function in both gaseous and condensed phases. In the gaseous phase, it employs chemical mechanism of redirection or termination of the chemical reactions involved in combustion<sup>6)</sup>, and physical mechanism of evolution of heavy bromine-containing gases which tend to protect the condensed phase by inhibiting access of oxygen and transfer of heat, it changes the route of the chemical reaction involved in decomposition.

Effect of the hydrogen bromide-containing melamine-formaldehyde condensates is depend on the content of bromine in the treated specimens. For HINOKI sliced veneer, self-extinguishing behavior requires about 2.5~2.95% of bromine. The contribution of bromine is even more significant, as can be seen in the results shown in Table 2 and the plot of char length vs resin add-ons in the specimens (Figs. 1, 2, 4 and 5), comparing the efficiencies of Br-containing resin and Cl-containing one.

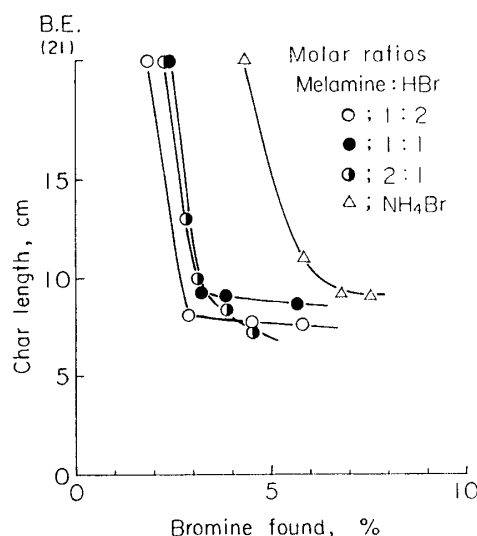


Fig. 3. Char length as a function of bromine content in HINOKI sliced veneer. (B.E.=Burned Entire Length)

As shown in and Fig. 3, in the hydrogen bromide-containing melamine-formaldehyde condensates treated HINOKI sliced veneer, a 10 cm char length was obtained at somewhat lower bromine contents than in the case of the ammonium bromide treated one. From these char-length data, it is obvious that melamine also assist in conferring for fire resistance.

#### *Hydrogen chloride-containing melamine-formaldehyde condensation products*

In Fig. 4 the char length of HINOKI sliced veneer treated with solutions of varying amounts of the hydrogen chloride-containing melamine-formaldehyde condensate are shown. For HINOKI sliced veneer, it is apparent that fire proofing

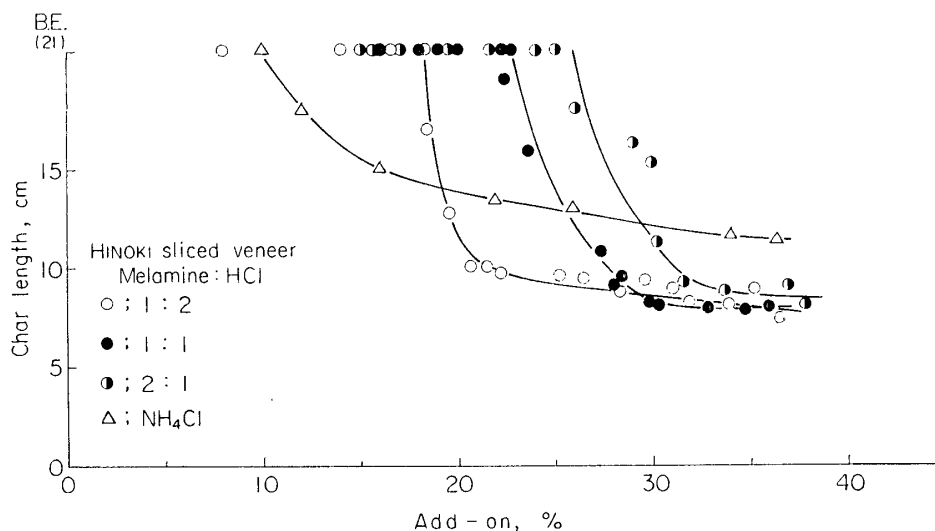


Fig. 4. Effect of HCl-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/HCl molar ratios. (B.E.=Burned Entire Length)

efficiency of this resin is depend on the ratios of hydrogen chloride to melamine. Using of the equimolar hydrogen chloride to melamine, char-length values approach less than 10 cm as the percentage of the resin in specimens reached to to above 18%. And char length data for filter paper treated with these resins are shown as a function of resin-add-on, in Fig. 5. Comparison of results of filter paper and HINOKI sliced veneer suggests that a lower resin add-on is sufficient to reach a 10 cm char length for filter paper. The fire proofing efficiency of filter paper did not depend on the ratio of hydrogen chloride to melamine. Although they are not completely conclusive, the results that efficiencies of filter paper differed from that of HINOKI sliced veneer were shown in Fig. 4 and Fig. 5.

Chlorine is believed to perform its flame retardant function, like bromine, in in both the gaseous and condensed phases according to two mechanisms as described above.

As shown in Figs. 1, 2, 4 and 5 and Table 2, the chlorine-containing melamine-formaldehyde condensation product was less effective than bromine-containing one in both HINOKI sliced veneer and filter paper. In the case of the equimolar resin of melamine and hydrogen halides, comparisons of relative effectiveness of the bromine-containing resin and the chlorine-containing one indicate that about 10% add-on of the former is equivalent of about 27~28% of the latter in HINOKI sliced veneer.

The effectiveness of halogens on the burning properties of cellulosic materials varies with molar ratio of hydrogen halides to melamine. As shown in Figs. 1



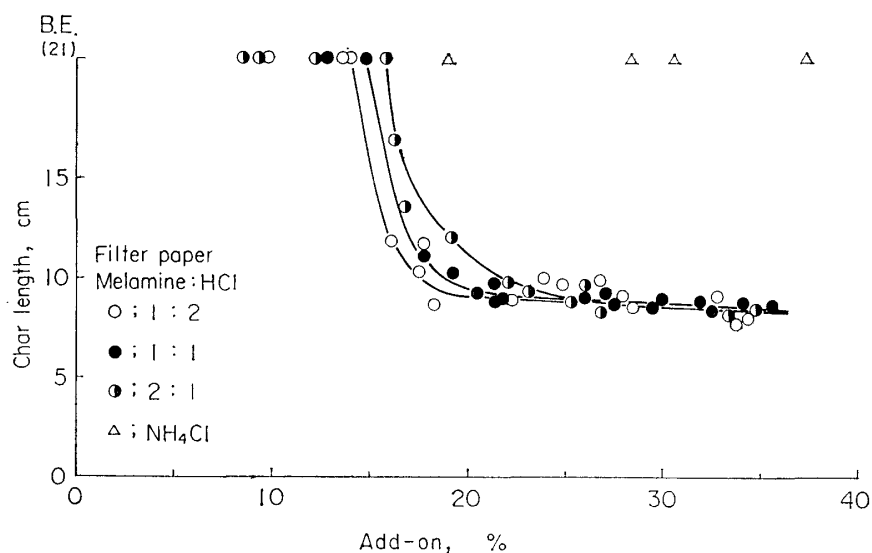


Fig. 5. Effect of HCl-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/HCl molar ratios. (B.E.=Burned Entire Length)

and 4, the higher molar ratio of the hydrogen halide to melamine is more effective than the lower ratio in HINOKI sliced veneer.

In this experiment, hydrogen chloride and hydrogen bromide were used, as described above, the latter is about twice or more as efficient on a weight basis as the former. Table 2 lists minimum quantities of chlorine and bromine compounds necessary to prevent flaming combustion for both HINOKI sliced veneer and filter paper. The greater effectiveness of bromine is clearly demonstrated, on

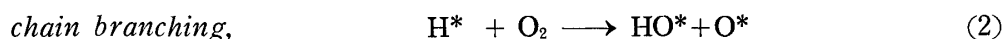
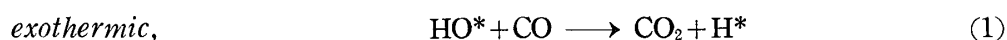
Table 2. Minimum quantity of hydrogen halides-containing melamine-formaldehyde resins, and halides necessary to prevent flaming combustion for HINOKI sliced veneer and filter paper\*.

Moles hydrogen halide per mole melamine		Weight percentage of resin		Weight percentage of halide (found)		Molar percentage of halide	
		HINOKI	Filter paper	HINOKI	Filter paper	HINOKI	Filter paper
2:1	HBr	6.0	10.1	2.9	4.9	3.6	6.1
	HCl	20.6	18.8	6.1	5.7	17.2	15.9
1:1	HBr	10.5	11.0	3.5	3.6	4.3	4.4
	HCl	27.5	20.1	4.8	3.5	13.5	8.5
1:2	HBr	16.5	17.0	3.2	3.3	3.95	4.1
	HCl	31.0	22.3	2.9	2.2	8.2	6.2
NH <sub>4</sub> Br		8.5	9.0	6.9	7.4	8.2	9.2
NH <sub>4</sub> Cl		33.8	60.0 over**	22.5	39.8 over**	63.5	112**

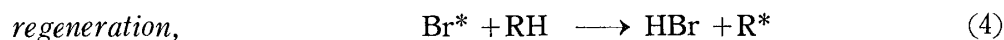
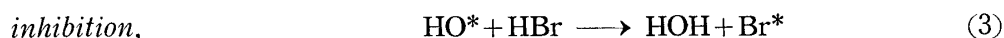
\* No samples showed after glow with exception of the B.E.\*\* sample.

\*\* Burned entire length.

an atom by atom basis. It has been shown by V. A. Stenger and G. J. Atchison<sup>7)</sup> that one atom of bromine is as effective in reducing flammability as two of chlorine. This table seems at least qualitatively, to support their view. The probable reasons for these are found in the differences of the bond energy and of the molecular weight. As the bond strength of hydrogen bromide is less than that of hydrogen chloride, inhibition reaction of flame combustion would progress more slowly with hydrogen chloride. And the chlorine-containing vapors, for example, hydrogen chloride are more volatile and lighter than the corresponding bromine compound, and can be expected to have a shorter residence time in combustion zone. These observations explain why bromine should be more effective than chlorine. This mechanism was clarified by W. A. Rosser<sup>8)</sup>, H. B. Palmer<sup>9)</sup> and C. F. Cullis<sup>10)</sup>. Combustion in flames is believed to proceed by branching chain reactions among free radicals. In flames, most important reactions are probably as follows:



Hydrogen is formed in exothermic reaction and is used in branching chain reaction. The HO\* radical is formed in reaction (2) and used in reaction (1). A branching chain reaction is thereby initiated and attempts can be made to interrupt it by reducing the concentrations of radicals such as H\* and HO\*. At flame temperatures the halogens dissociate to atoms which combine with radicals essential to the process of combustion in flame, after which the new combination yields a stable molecule, or at least less reactive radical and regenerates the halogen to repeat the process<sup>8,10)</sup>. Halogens such as hydrogenbromide and bromine from bromine compounds interact with the highly reactive HO\* radical to give the following reaction:



RH is an organic compound containing hydrogen. The practical result is that HO\* is replaced by a less reactive species such as Br\* or R\* and branching chain reaction ceases in consequence.

#### *Ammonium salts*

Fig. 6 the char length data for HINOKI sliced veneer treated with ammonium salts are shown, as a function of chemical content. If one assumes that the shorter the char length, the better the fire proofing properties, then from this figure it appears that diammonium hydrogen phosphate is the best. Ammonium bromide

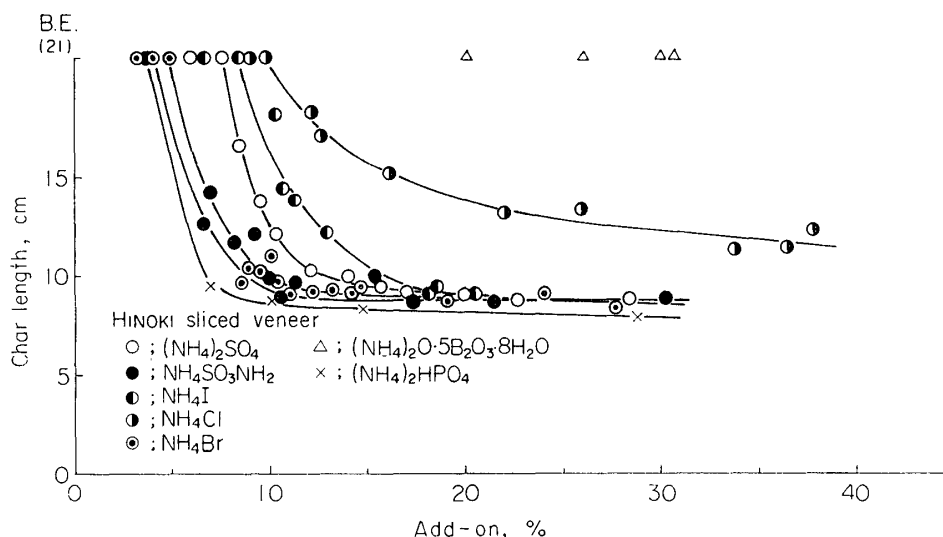


Fig. 6. Relative fire-proofing efficiencies of water soluble ammonium salts based on char length.  
(B.E.=Burned Entire Length)

and ammonium sulfamate are about as excellent as diammonium hydrogen phosphate, but are not quite equal to ammonium phosphate for HINOKI sliced veneer. Ammonium sulfate and ammonium iodide are also similar to ammonium phosphate. As described above, ammonium halides are, as flame retardant, effective for wood<sup>12)</sup> and cellulosic materials<sup>13)</sup>. Comparison of results obtained in the application of both ammonium bromide and ammonium chloride shows that quite a higher chemical content is required to reach a certain char length in the case of the latter. From Figs. 6 and 7 it will be seen that effect of ammonium chloride was quite small compared to that of the other ammonium salts with an exception of ammonium pentaborate. Ammonium chloride and its pyrolytic products, however, are lighter than their bromids and iodine analogues, so that their fire retardant effect is inferior. Ammonium pentaborate appear ineffective when alone.

In Fig. 7 the char length data of filter paper treated with the same aqueous solution as described above are shown. From this figure it appears that the behavior of these salts as fire retardant for filter paper is very similar to that of HINOKI sliced veneer. These ammonium salts with exceptions of the lower retention levels of ammonium chloride and of ammonium pentaborate imparted good glow resistance to both HINOKI sliced veneer and filter paper. This experimental data indicate that the effectiveness of ammonium salts as fire retardant for HINOKI sliced veneers increases in the order of ammonium pentaborate, ammonium chloride, ammonium iodide, ammonium sulfate, ammonium sulfamate, ammonium bromide and ammonium phosphate. This trend can be found in filter paper as quite the same

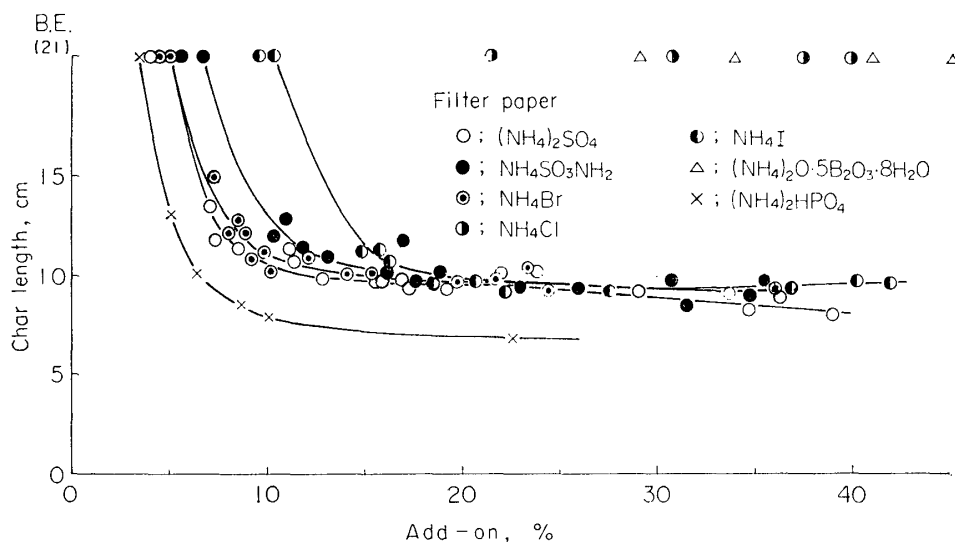


Fig. 7. Relative fire-proofing efficiencies of water soluble ammonium salts based on char length.  
(B.E. = Burned Entire Length)

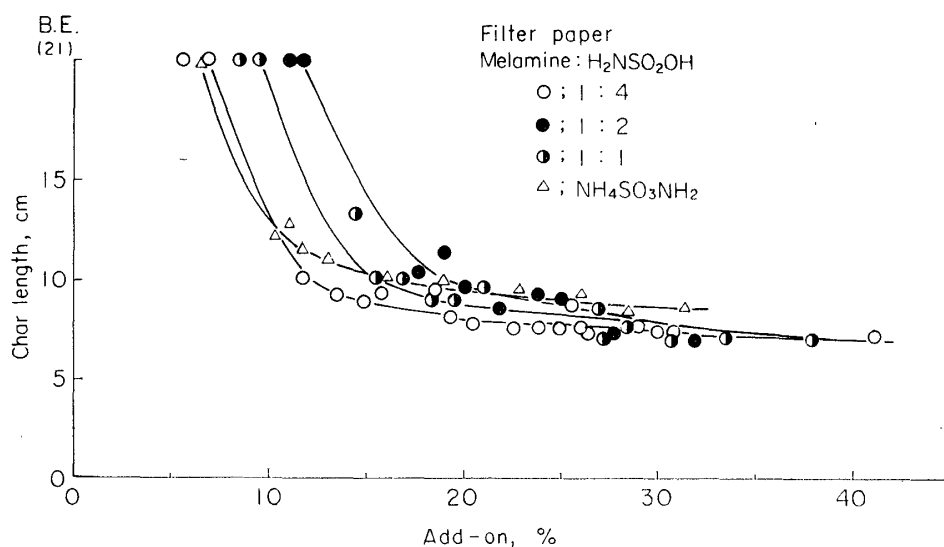


Fig. 8. Effect of  $\text{H}_2\text{NSO}_2\text{OH}$ -containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/ $\text{H}_2\text{NSO}_2\text{OH}$  molar ratios.  
(B.E. = Burned Entire Length)

as HINOKI sliced veneer. These experimental results are in close agreement with many investigation results which have been made on these inorganic compounds since old time<sup>14~16)</sup>.

*Sulfuric acid-containing melamine-formaldehyde condensation products and sulfamic acid-containing ones.*

Figs. 8 and 10 show the char length data of filter paper treated with acidic melamine-formaldehyde condensates with various molar ratios of sulfamic acid

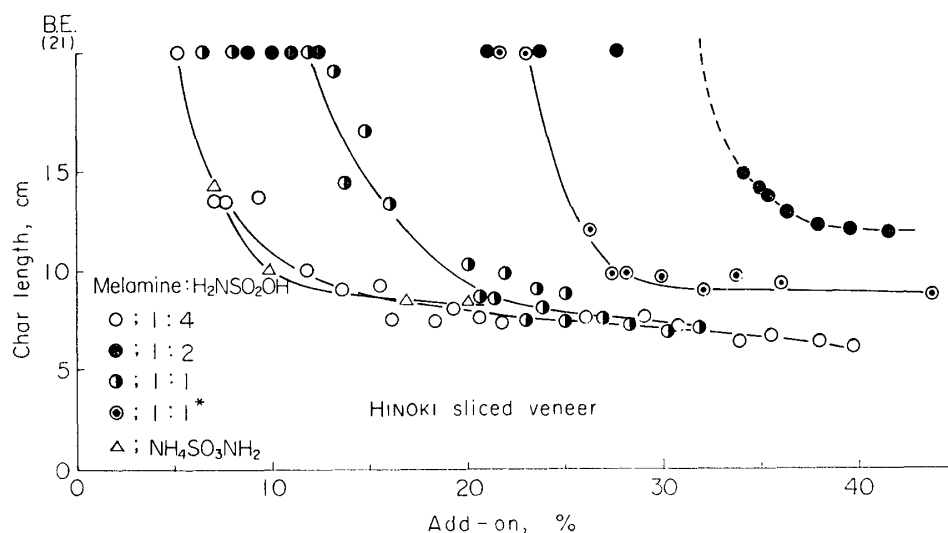


Fig. 9. Effect of  $\text{H}_2\text{NSO}_2\text{OH}$ -containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/ $\text{H}_2\text{NSO}_2\text{OH}$  molar ratios.  
\* Treating resins were impregnated in a vacuum (20 mmHg) for 10 min.  
(B.E.=Burned Entire Length)

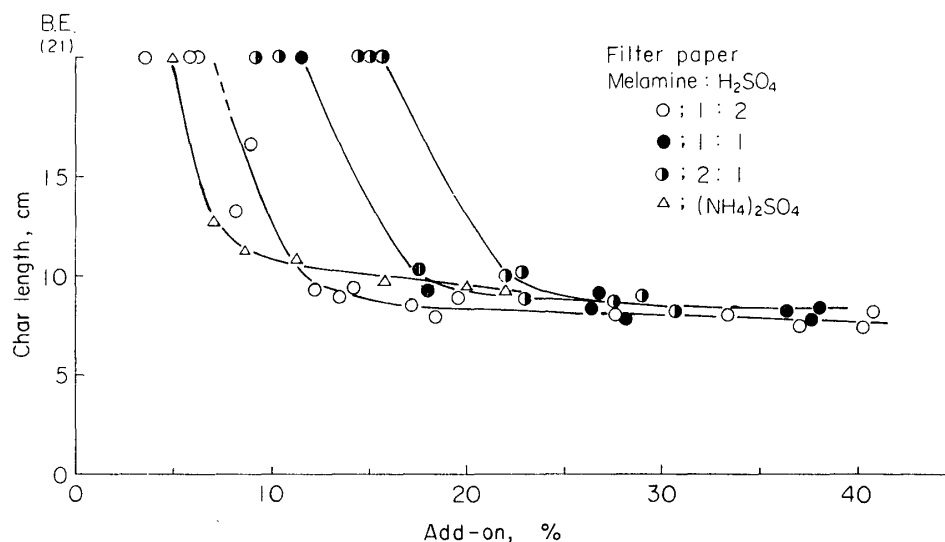


Fig. 10. Effect of  $\text{H}_2\text{SO}_4$ -containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/ $\text{H}_2\text{SO}_4$  molar ratios.  
(B.E.=Burned Entire Length)

and of sulfuric acid to melamine, respectively. From these figures, it is obvious that there is a steady increase in fire proofing efficiencies with an increased molar ratios of acids to melamine in the treating solution. This trend can be found in HINOKI sliced veneer as well as in filter paper as shown in Figs. 9 and 11. Char length data show that somewhat higher add-on of the resins, are required to reach a given char length in the case of HINOKI sliced veneer compared to filter paper.

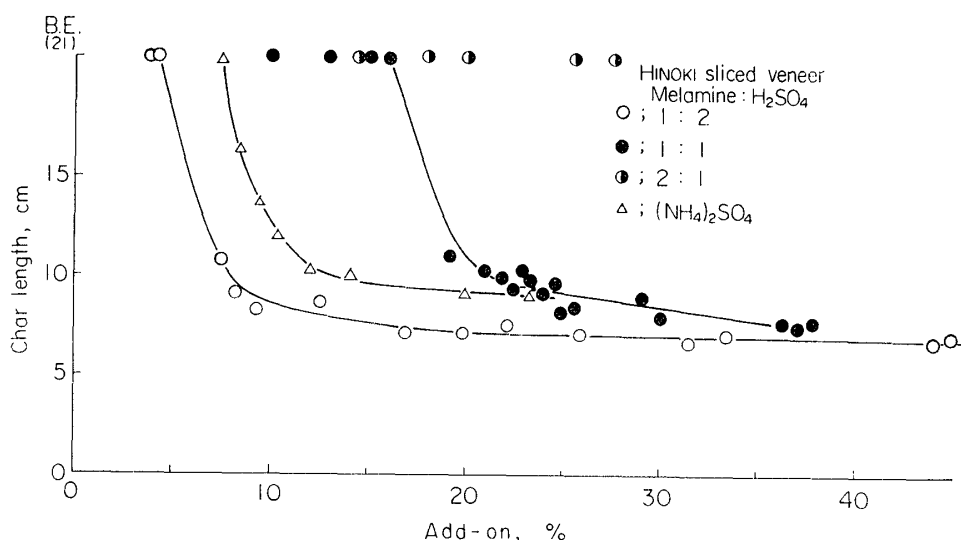


Fig. 11. Effect of H<sub>2</sub>SO<sub>4</sub>-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/H<sub>2</sub>SO<sub>4</sub> molar ratios. (B.E. = Burned Entire Length)

A considerable difference, however, using the treating solutions of lower acid molar ratios, is evident in the fire proofing efficiencies of HINOKI sliced veneer and filter paper.

In the treatments with the higher acid molar ratios of resins (melamine/H<sub>2</sub>NSO<sub>2</sub> OH : 1/4 and melamine/H<sub>2</sub>SO<sub>4</sub> : 1/2, respectively), a 8.8 cm char length of both HINOKI sliced veneer and filter paper was obtained at somewhat lower add-on of of fire retardant than in the cases of the corresponding ammonium salts. These sulfur-containing strong acids such as sulfamic and sulfuric acid combined with methylolmelamine imparted good fire resistance. This trend can be found in other methylol derivatives of amines and amides such as urea, dicyandiamide and the like<sup>17)</sup> as well as melamine. However, efficiencies of these acid-containing resin were less than that of phosphoric acid-containing ones described previously<sup>4)</sup>.

Both sulfamic and sulfuric acids-containing melamine-formaldehyde condensates have been found useful. Presumably, the materials decomposes on heating to leave concentrated acids behind. These acids then participate much as does phosphoric acid to change the route of thermal decomposition of cellulose and wood<sup>21)</sup>. And combustion in flame is inhibited by a suitable acidic catalyst<sup>18,23,24)</sup> released at combustion temperatures by decomposition of these acids-containing resins.

#### *Boric acid-containing melamine-formaldehyde condensation products*

Char length data for HINOKI sliced veneer treated with boric acid-containing melamine-formaldehyde condensates are shown, as a function of resin add-on in

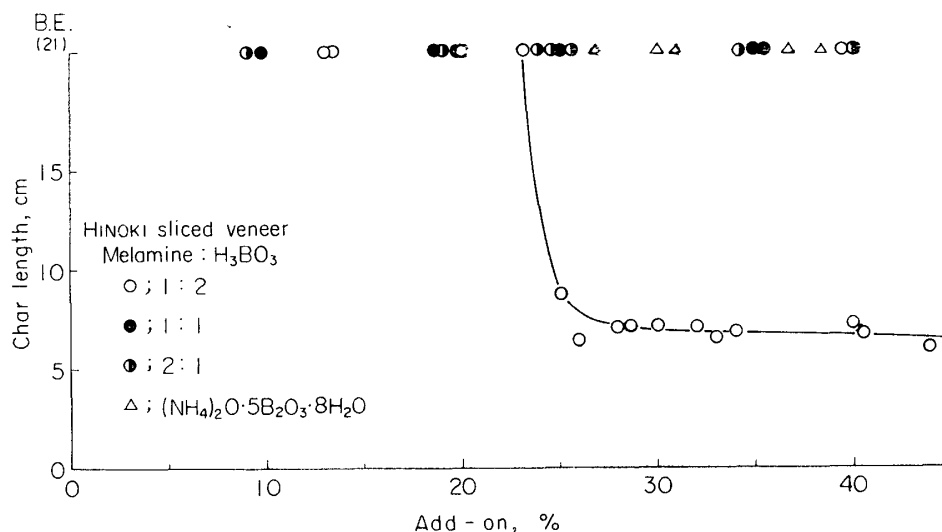


Fig. 12. Effect of H<sub>3</sub>BO<sub>3</sub>-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/H<sub>3</sub>BO<sub>3</sub> molar ratios. (B.E.=Burned Entire Length)

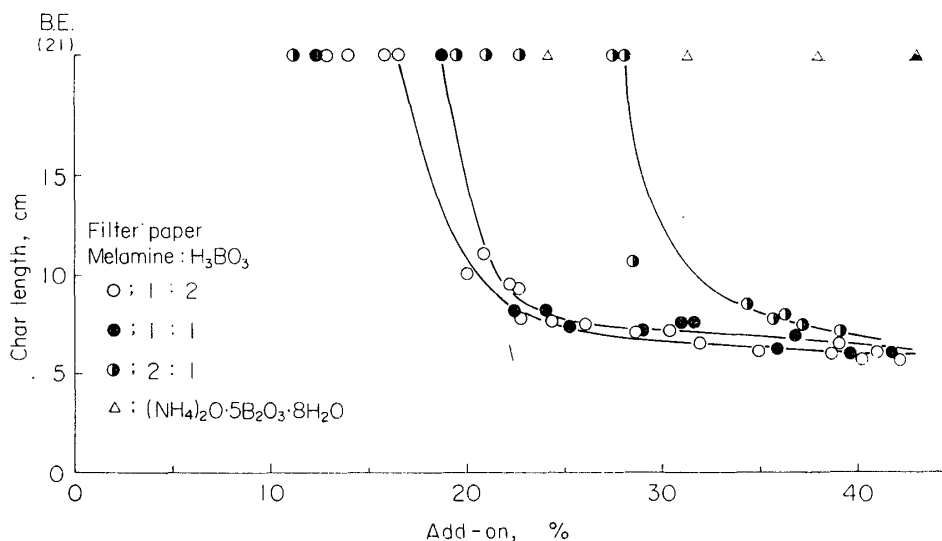


Fig. 13. Effect of H<sub>3</sub>BO<sub>3</sub>-containing melamine-formaldehyde condensates on their fire-proofing efficiency at various melamine/H<sub>3</sub>BO<sub>3</sub> molar ratios. (B.E.=Burned Entire Length)

in Fig. 12. For HINOKI sliced veneer, boric acid-containing melamine-formaldehyde resins with exception of one with a higher molar ratio of boric acid, did not have adequate fire resistance and burned completely when tested by the vartical flame test.

For HINOKI sliced veneer treated with a solution of higher acid molar ratio, char length approached less than 10 cm at above 25% resin. In wooden materials, the use of boric acid-containing aminotriazine-aldehyde resin alone is not feasible

because of the higher levels required<sup>22)</sup>.

In Fig. 13 char-length values of filter paper treated with the solution of these resins are plotted against resin add-on. It is apparent that higher retention levels of all resins with the various molar ratios of components affect the flammability of filter paper unlike HINOKI sliced veneer. The difference of the burning properties of HINOKI sliced veneer and filter paper treated with the same resins, is not clear from the results of this study. The effectiveness of these resins as fire retardant are influenced by the molar ratios of boric acid to melamine. For filter paper containing no other synergist such as alkali metals, in case of the resin in which boric acid is equimolar to melamine, self-extinguishing behaviour (char length is less than 8.5 cm) required about 22.5 to 24% resin. It is obvious that boric acid-containing melamine-formaldehyde condensates alone is less effective than the other acids-containing ones as described above.

Boron-containing compounds were believed, in general, to perform most of its flame retardant function in the condensed phase. Boron containing fire retardants such as boric acid, borate and metaborate increase the amount of char formed, due to one or both of two mechanisms: redirection of chemical reactions involved in thermal decomposition in favour of reaction yielding carbon rather than carbon monoxide and carbon dioxide<sup>19)</sup>, and formation of glassy surface layer of protective char which prevents gasification of the carbon by blocking access of oxygen required. The chemical influence of boron may involve removal of vulnerable hydroxyl groups of cellulose and other components of wood by dehydration<sup>20)</sup>.

Boric acid melts at 170.9°C<sup>20)</sup>, a temperature too low to make it an effective fluxing agent, and it does not have the action of dehydration<sup>21)</sup> alike that of phosphoric acid. It is advisable to use jointly with some synergists<sup>22)</sup>.

Fig. 14 shows that the effect of the kind of acid on the char length values of HINOKI sliced veneer treated with the solutions with a higher acid molar ratio of resins (melamine/acid : 1/2). From this figure it is clear that fire proofing efficiencies of acid-containing melamine-formaldehyde condensates become higher in the order of boric acid, hydrochloric acid, sulfamic acid, surfuric acid, hydrobromic acid and phosphoric acid. This trend can be found in treatment of the lower acid molar ratios of resins as well as data in shown in Fig. 14. Fire proofing efficiencies of these cationic melamine-formaldehyde resins increased as the ratio of acid increased. From the experimental results as described above, it can be safely assumed that the fire proofing efficiencies of these resins are depend in general, on the amount of acid or acidic catalysts released at pyrolysis or combustion temperatures. However, comparison of char-length values of a given add-on of a resin and corresponding add-on of ammonium salt shows that the char length value of the former



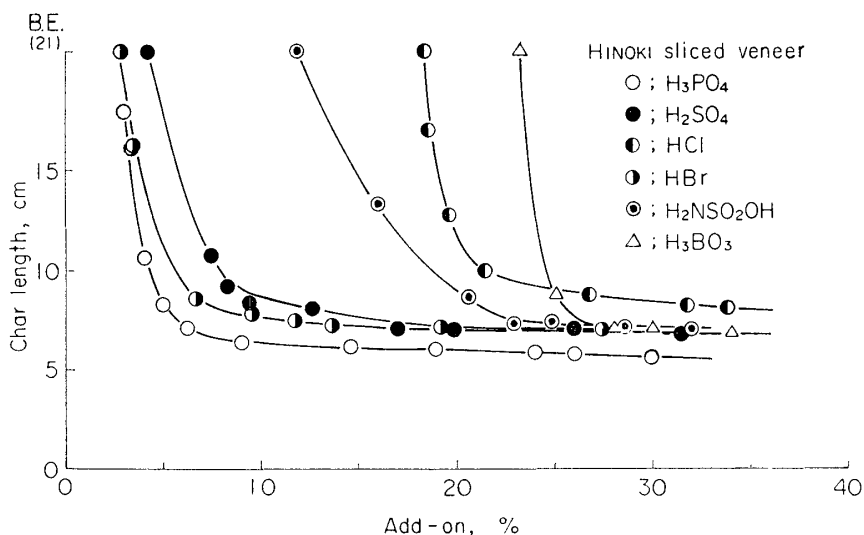


Fig. 14. Relative fire-proofing efficiencies of various acids-containing melamine-formaldehyde condensates at a component (melamine-acid) molar ratio of 1:2. (B.E.=Burned Entire Length).

is better than that of the latter in every cases. From the char-length data, it is obvious that melamine also assist in conferring for fire resistance and is not merely for the cross-linking agent.

Methylol derivatives of aminotriazines are flame retardant of themselves although these have not been shown clearly in many systems. When combined with other compounds that yields acids on heating, for examples, N-hydroxymethyl-3-(dialkylphosphono)propionamides<sup>23)</sup>, diallyl-2-cyanoethanephosphonate<sup>24)</sup>, boric acid-containing melamine-formaldehyde resin<sup>22)</sup>, and sulfamic acid<sup>25)</sup>, fire resistance is certainly observed.

### Summary and Conclusions

The durable fire retardant based on the colloidal solution of cationic melamine-formaldehyde resin have been applied to HINOKI sliced veneer and filter paper. They were prepared by the use of both inorganic acid and aminotriazine-aldehyde condensation product produced by conventional methods as starting materials.

This acid-containing aminotriazine-aldehyde condensation products give clear solutions in both neutral and acidic<sup>4)</sup>. This clear aqueous solution is converted upon aging, first to hydrophilic colloids, then to a water-dispersible gel, and finally upon drying to a water-insoluble resin. This aqueous solution impregnated in wood and filter paper is converted upon drying and curing for 5 weeks at room temperatures to a clear water insoluble resin.

The process is accomplished by soaking samples through an aqueous solution

of this resin, drying and curing at room temperatures.

In HINOKI sliced veneers and filter paper treated with the solution of higher acid molar ratios, fire resistance is attained at lower resin add-on than corresponding ammonium salts. Satisfactory fire proofing properties can be obtained in both HINOKI sliced veneer and filter paper at resin add-on as low as about 10~15% with a few exceptions. Total amount of resin required becomes lower as melamine acid molar ratio is decreased.

Fire retardant effectiveness of these resins has been found to increase in the order of boric acid, hydrochloric acid, sulfamic acid, sulfuric acid, hydrobromic acid and phosphoric acid. A few differences of fire retardant effectiveness were observed between HINOKI sliced veneer and filter paper treated with the same solution.

Preparation of these cationic aminotriazine-aldehyde codensation products and its properties will be described in detail in coming report.

Chemical systems capable of imparting fire proofing properties to wood and cellulose, and synergistic effect of aminotriazines in the fire proofing effectiveness of acid-containing compounds or of other elements that yield acids on heating, will be the subject of further study.

### Acknowledgment

The authors express their appreciation to Messrs Y. KADOKAWA and N. OHBA for assistance in carrying out the experimental work. Thanks are also due to Mr. K. KIMOTO, NAIGAI Wood Industrial Co. Ltd. for supplying the HINOKI sliced veneer.

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